Cationic Group-IV Pincer-type Complexes for Polymerization and Hydroamination Catalysis

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Contents:

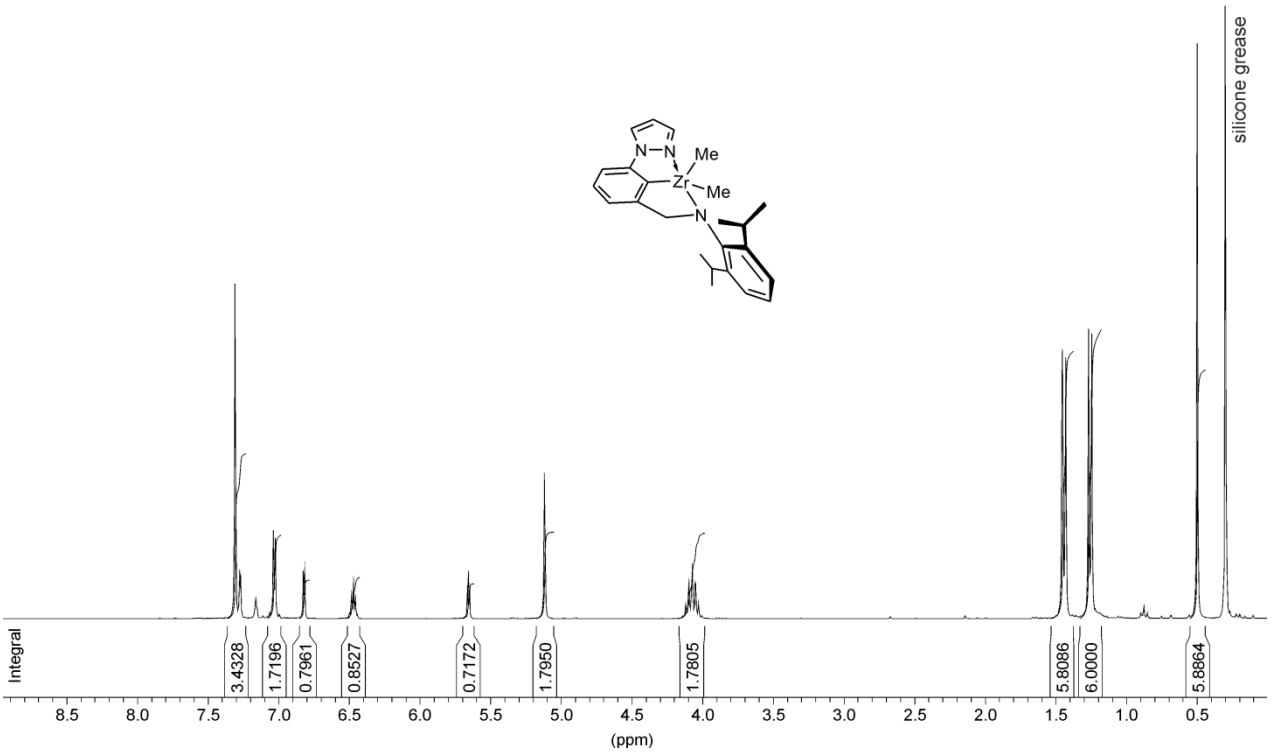


Fig. S1. ^{1}H-NMR spectrum (300 MHz, C_6D_6, 298K) of **3**.

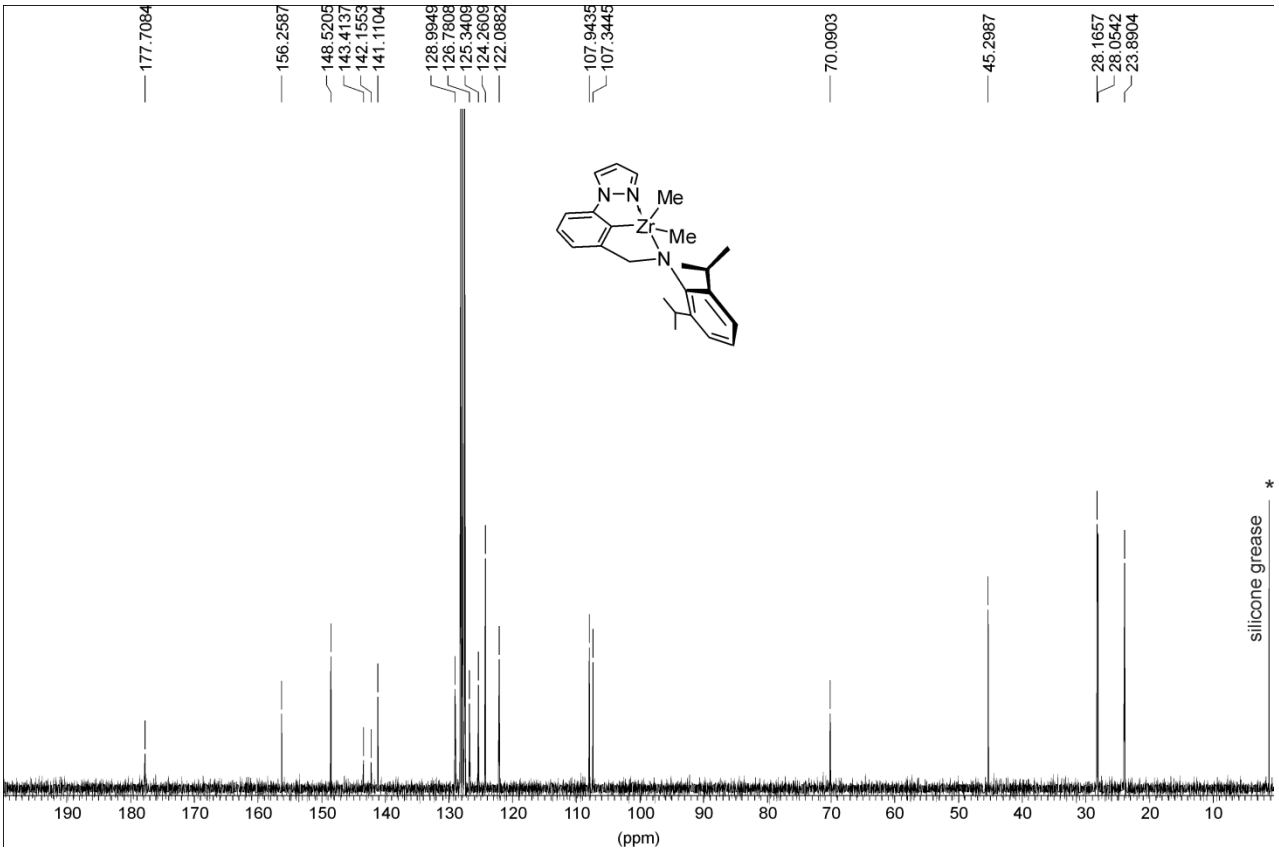


Fig. S2. ^{13}C{^{1}H}-NMR spectrum (75 MHz, C_6D_6, 298K) of **3**.

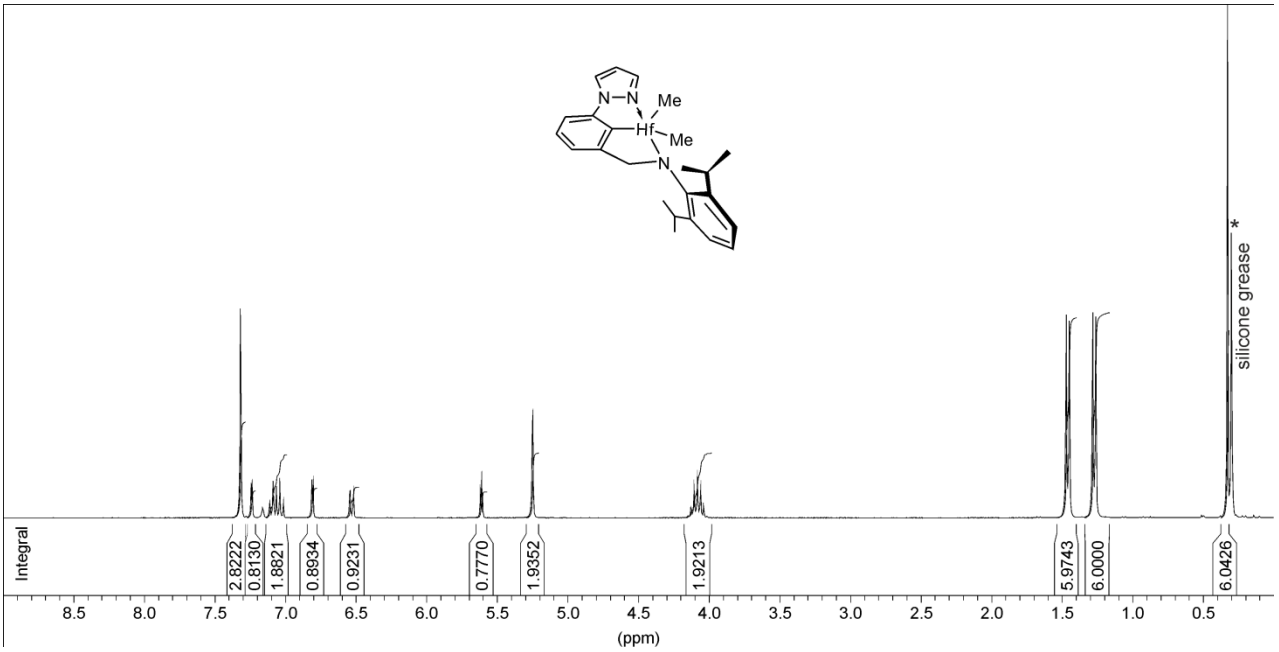


Fig. S3. ^{1}H-NMR spectrum (300 MHz, C_6D_6, 298K) of **4**.

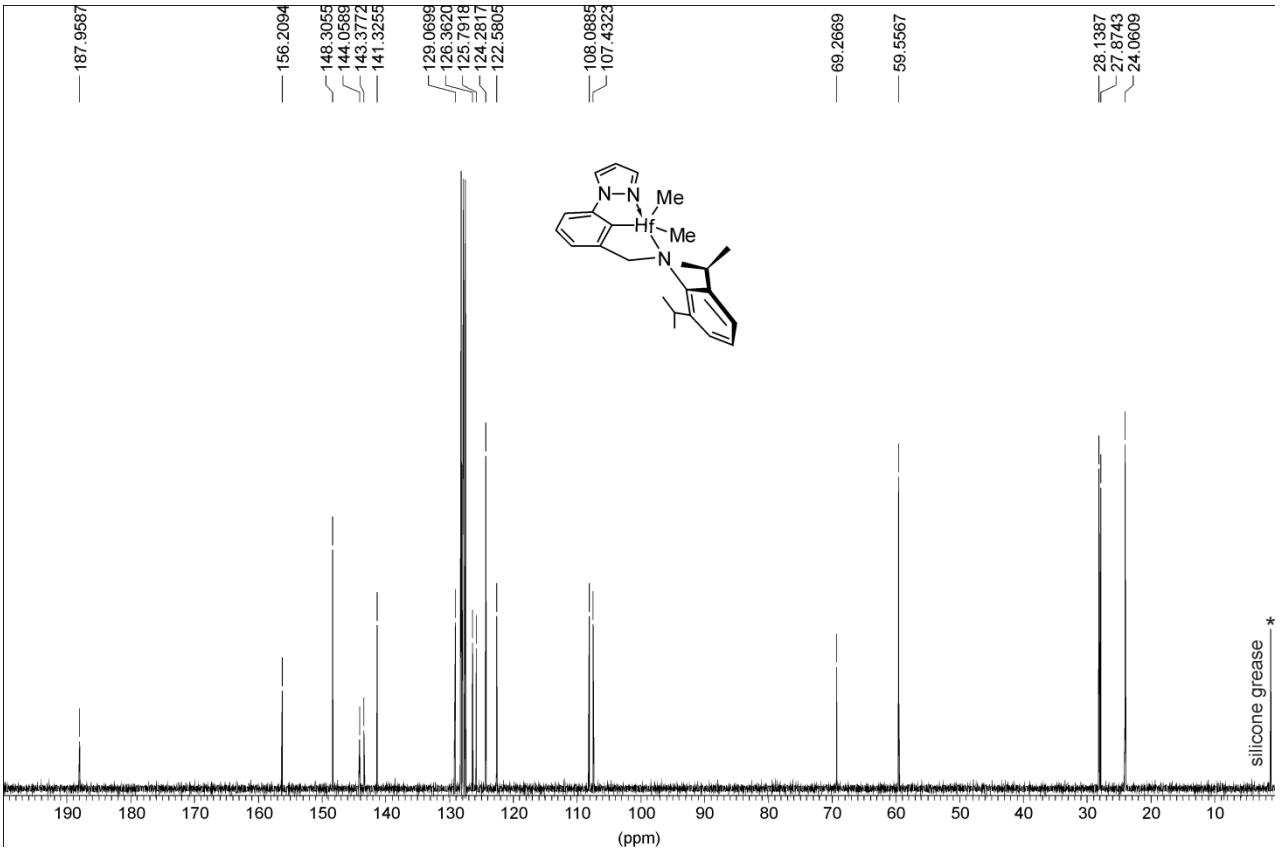


Fig. S4. ^{13}C{^{1}H}-NMR spectrum (75 MHz, C_6D_6, 298K) of **4**.

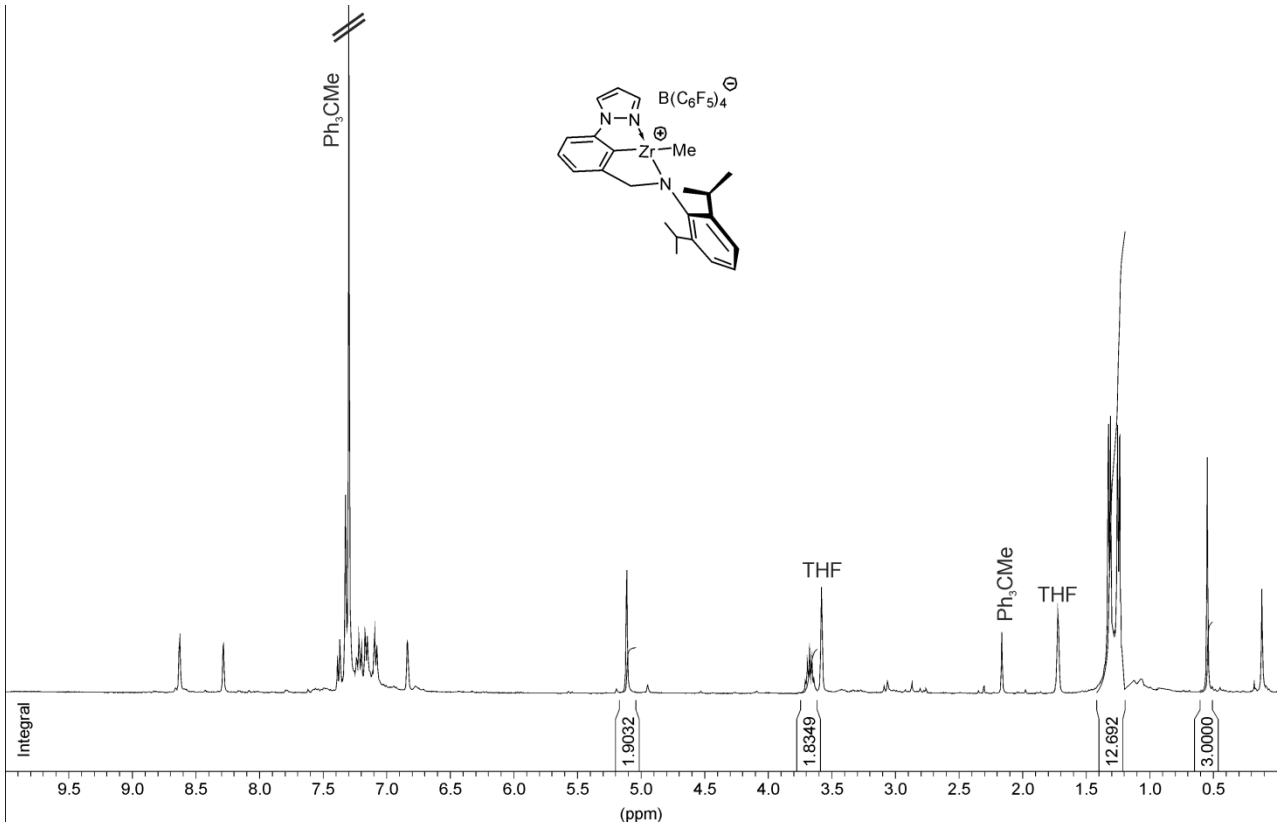


Fig. S5. ^{1}H-NMR spectrum (400 MHz, THF-$d_{8,}$ 298K) of **3a**.

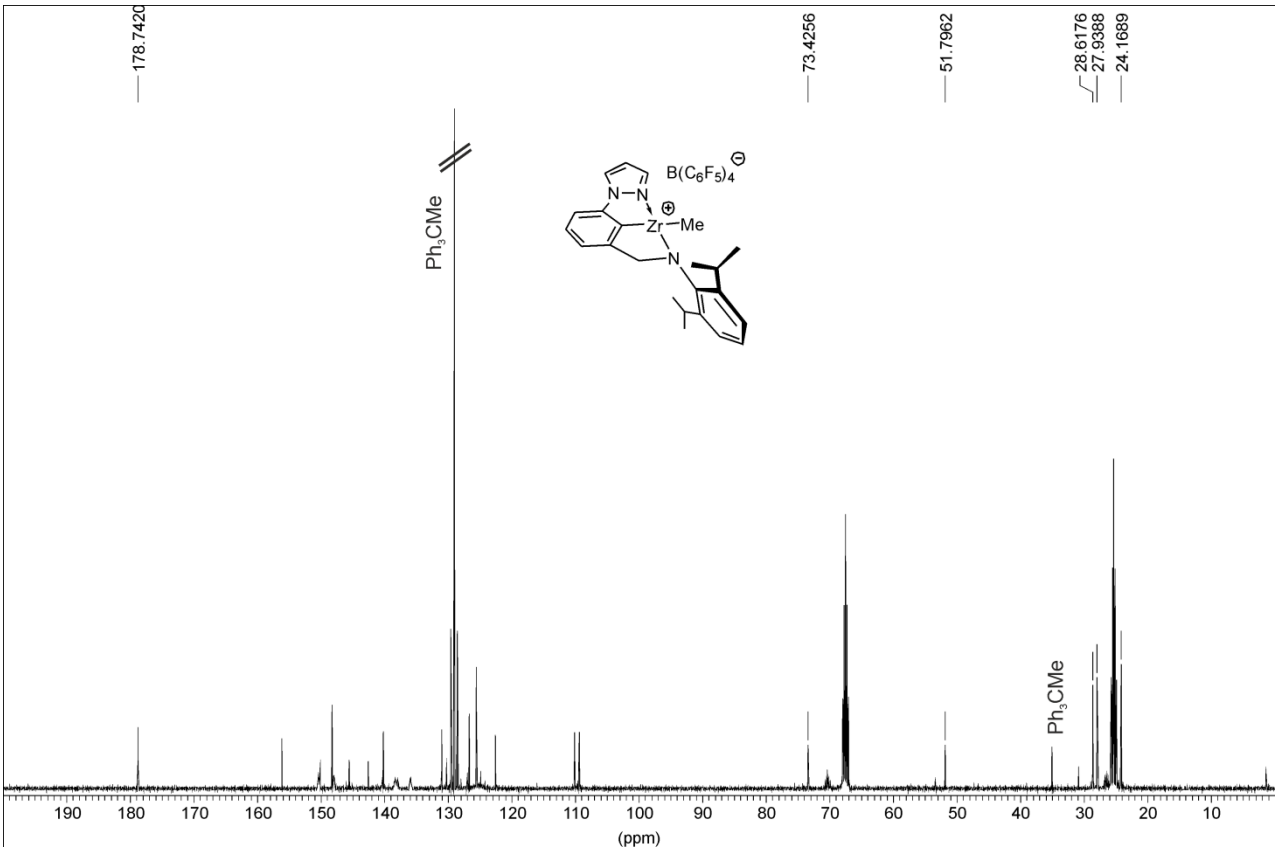


Fig. S6. ^{13}C{^{1}H}-NMR spectrum (100 MHz, THF-$d_{8,}$ 298K) of **3a**.

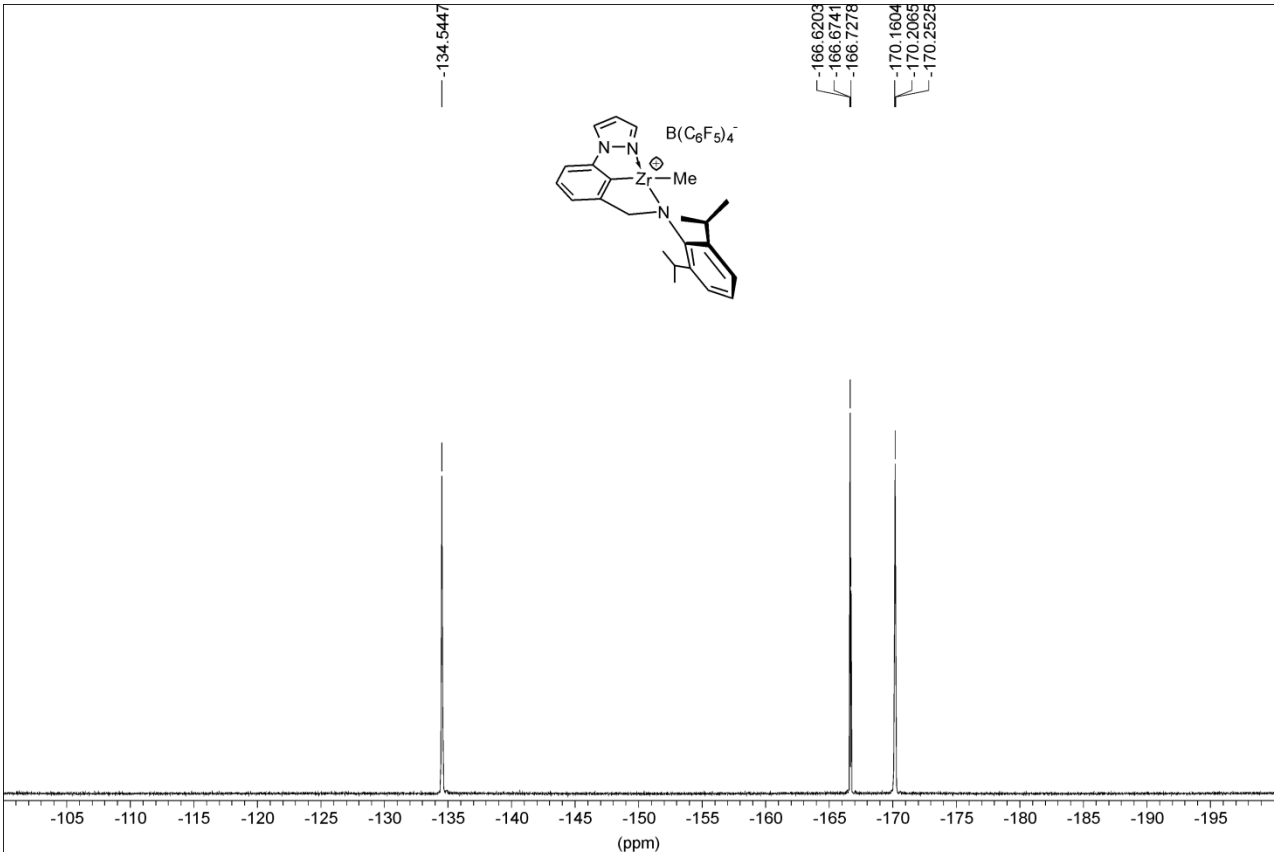


Fig. S7. $^{19}F\{^{1}H\}$-NMR spectrum (376.3 MHz, THF-d_8, 298K) of **3a**.

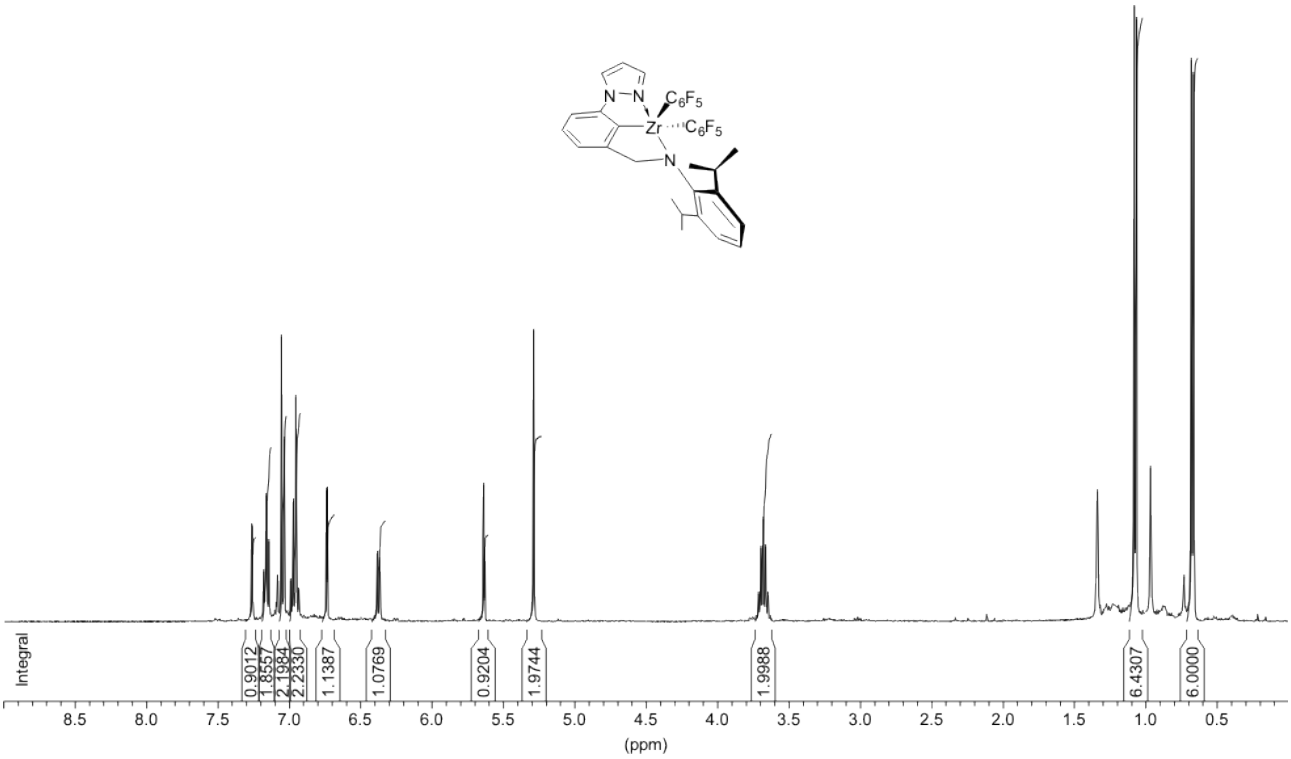


Fig. S8. ^{1}H-NMR spectrum (400 MHz, C_6D_6, 298K) of **3b**.

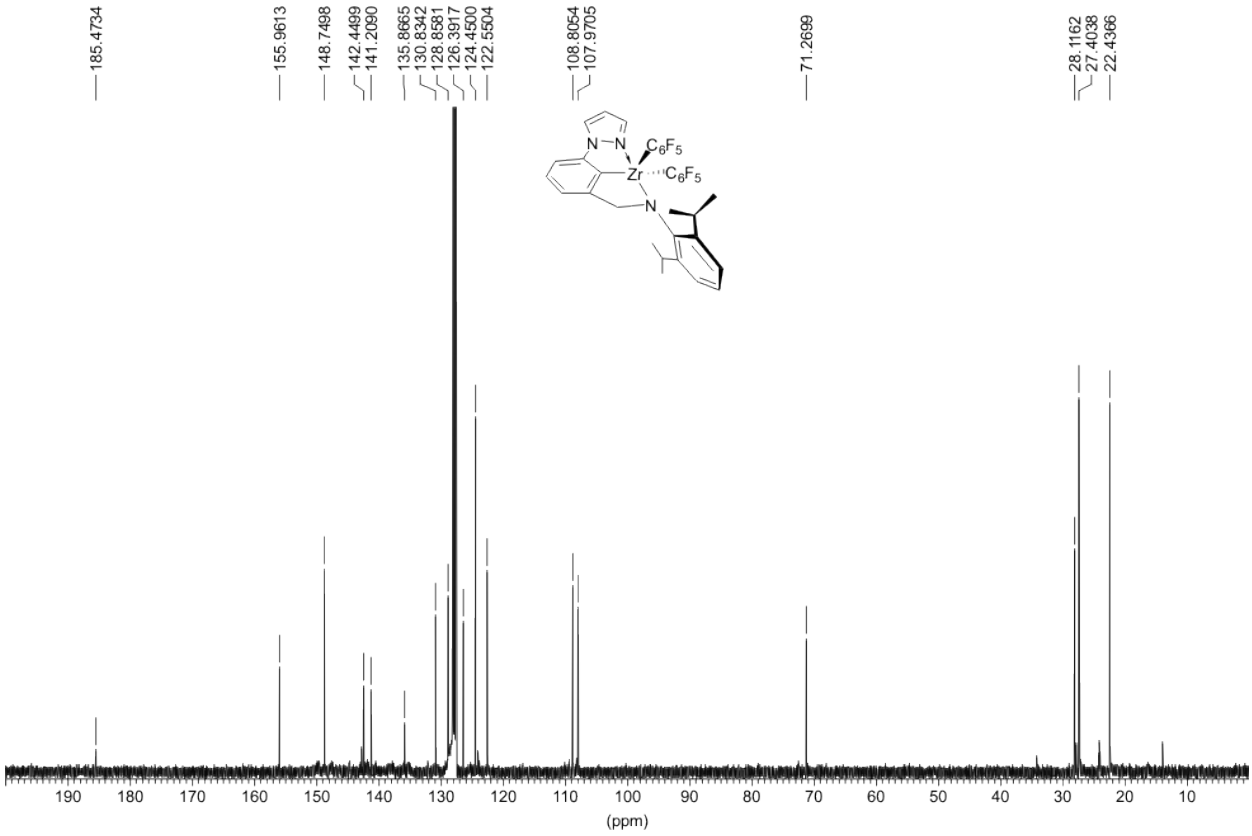


Fig. S9. $^{13}C\{^1H\}$-NMR spectrum (100 MHz, C_6D_6, 298K) of **3b**.

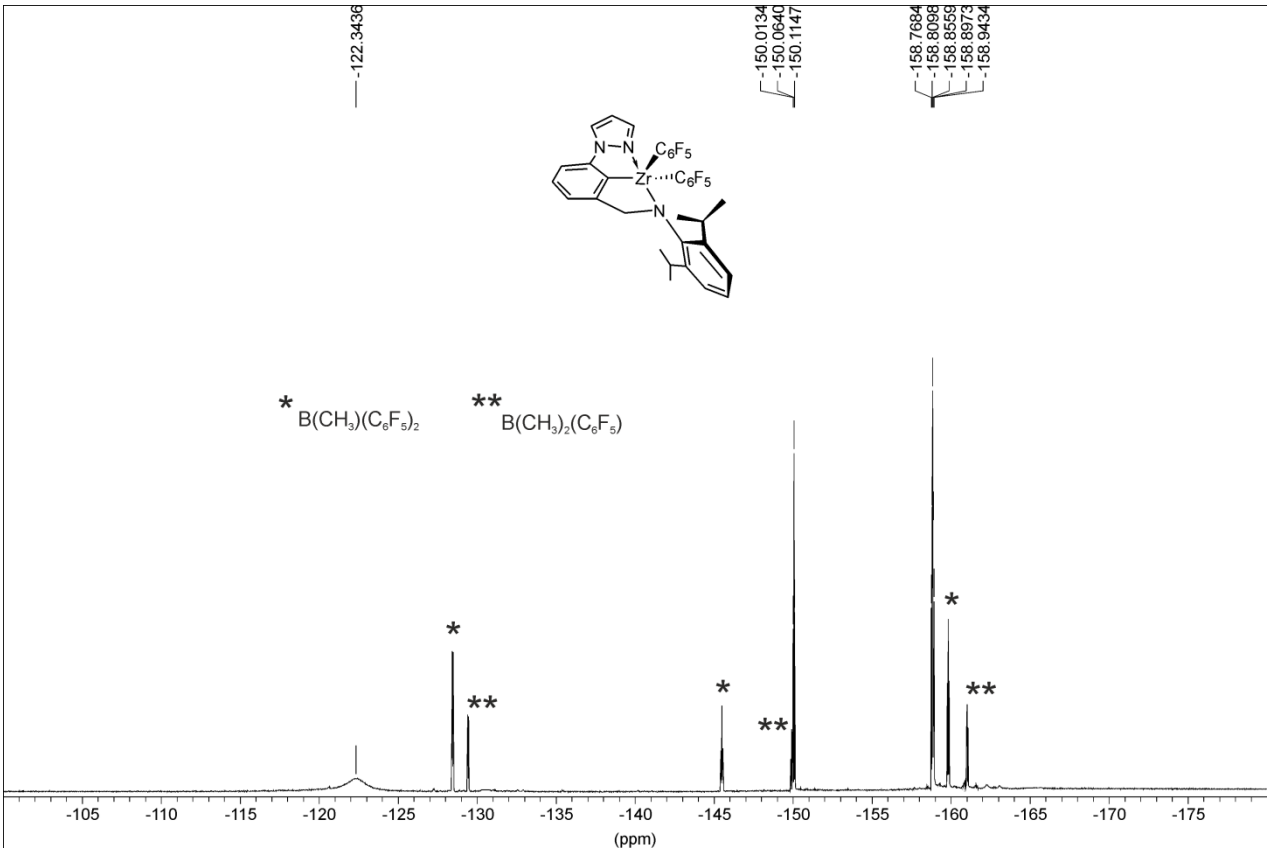


Fig. S10. $^{19}F\{^1H\}$-NMR spectrum (376.3 MHz, C_6D_6, 298K) of **3b**.

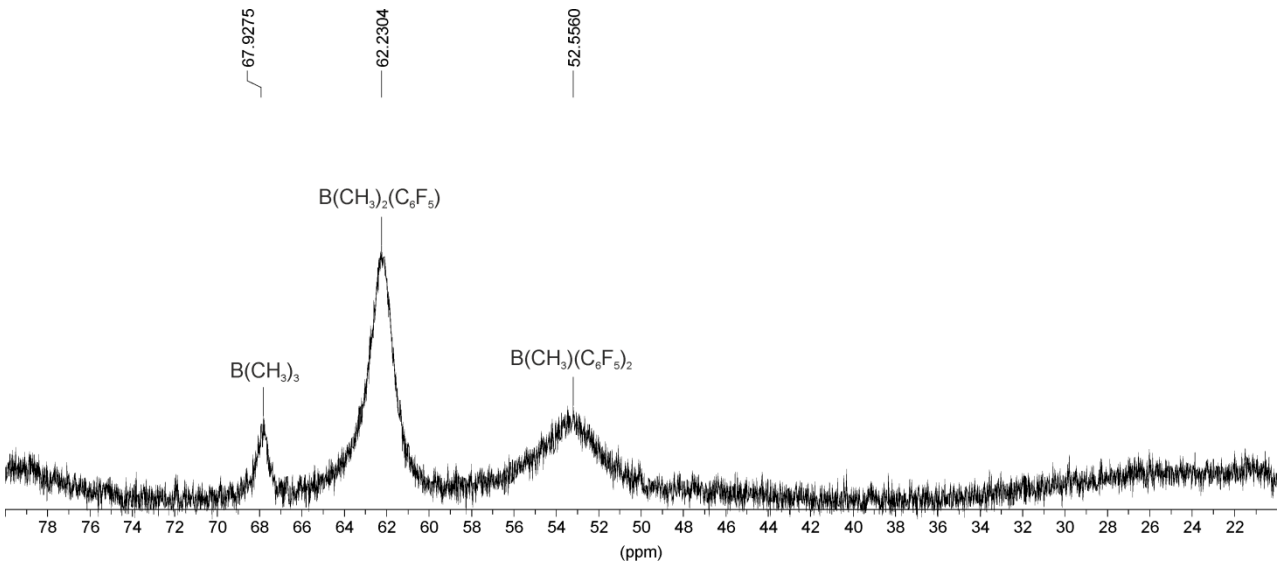


Fig. S11. $^{11}B\{^{1}H\}$-NMR spectrum (96.2 MHz, C_6D_6, 298K) of **3b**.

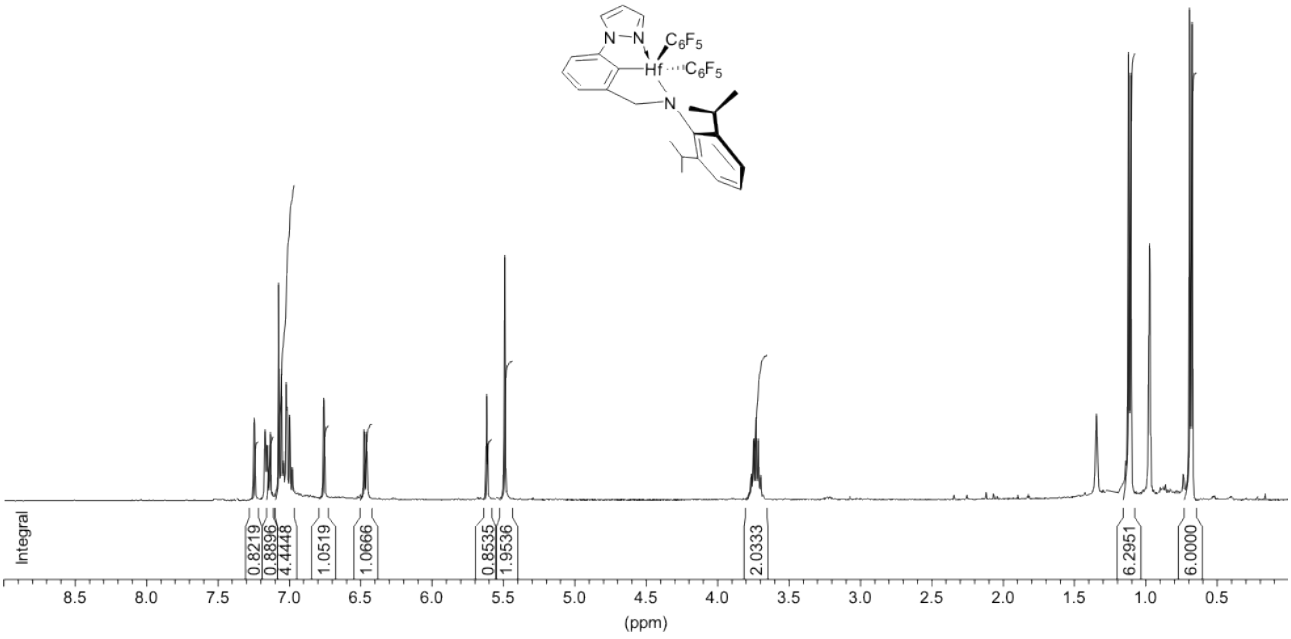


Fig. S12. ^{1}H-NMR spectrum (400 MHz, C_6D_6, 298K) of **4b**.

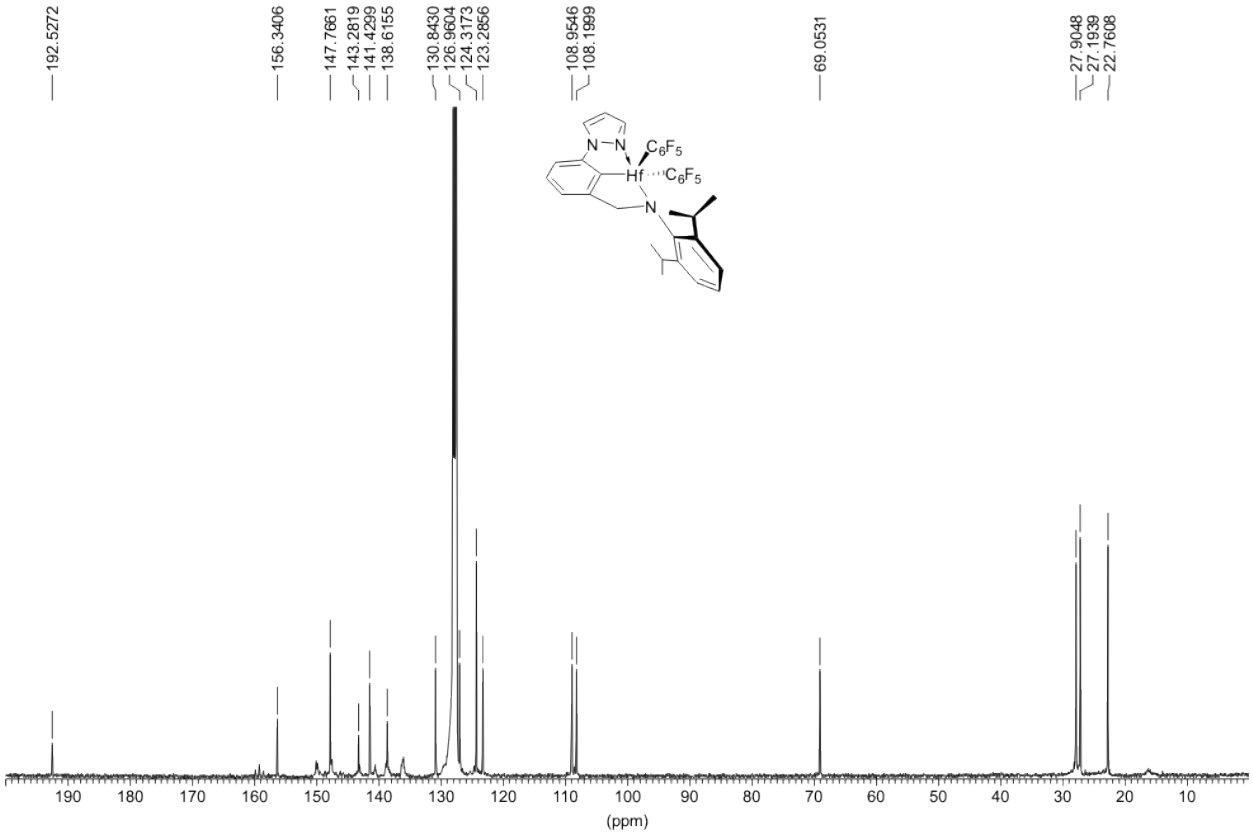


Fig. S13. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz, C_6D_6, 298K) of **4b**.

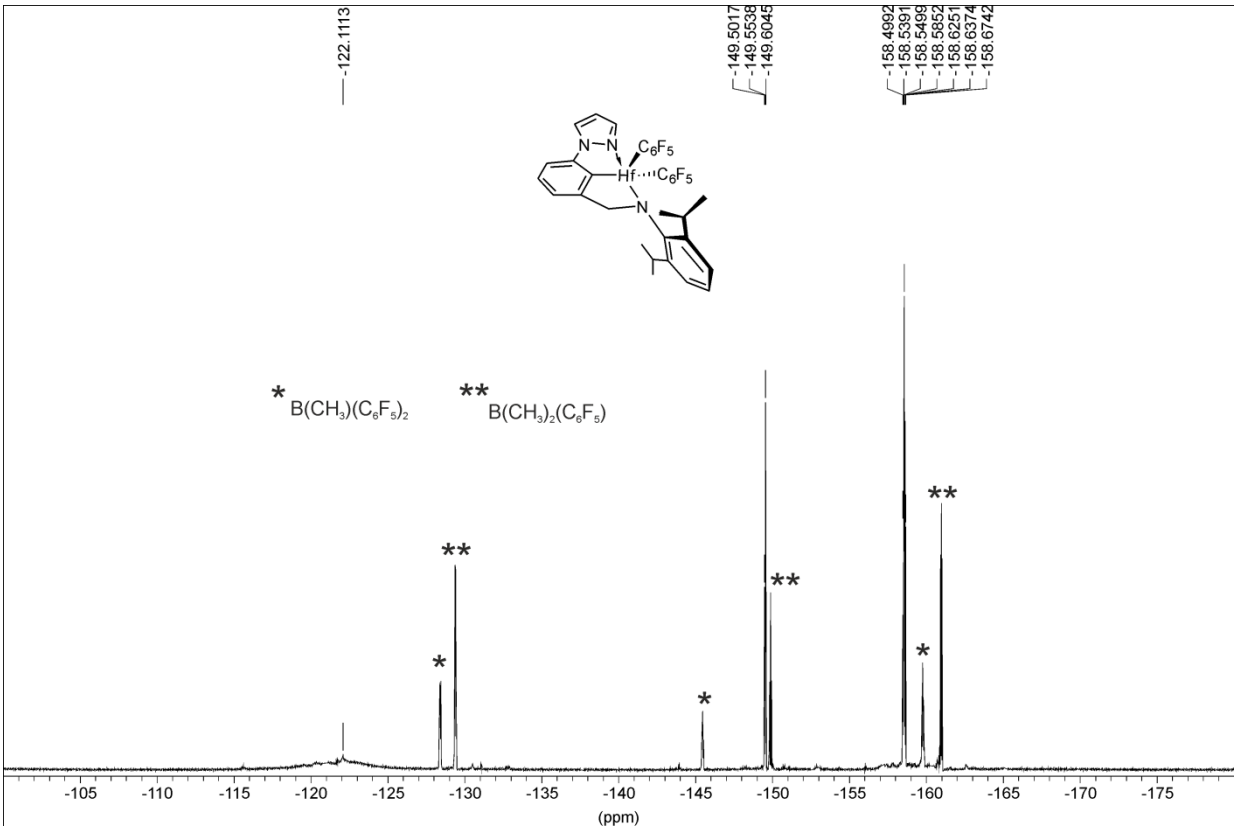


Fig. S14. $^{19}F\{^{1}H\}$-NMR spectrum (376.3 MHz, C_6D_6, 298K) of **4b.**

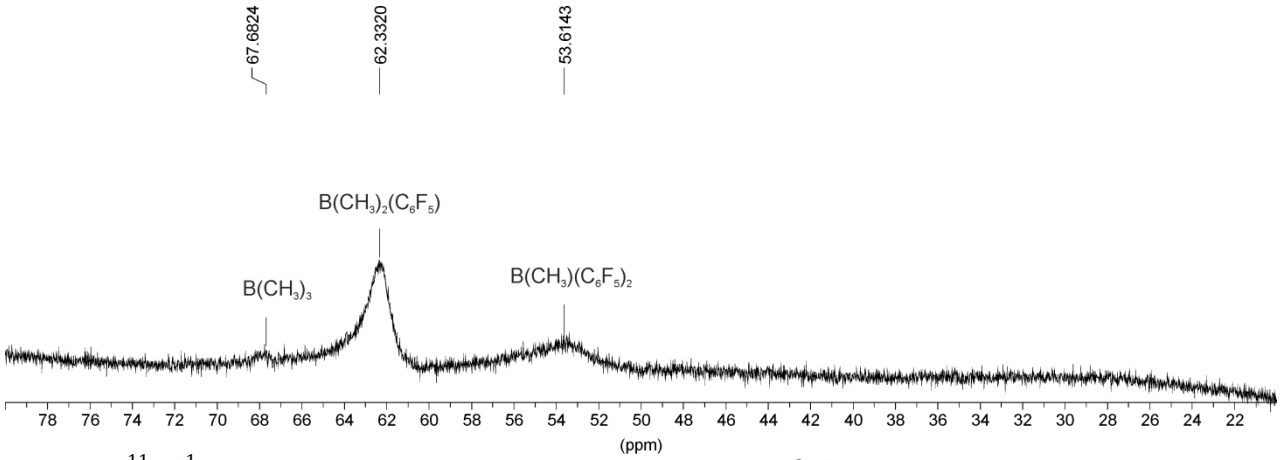


Fig. S15. $^{11}B\{^{1}H\}$-NMR spectrum (96.2 MHz, C_6D_6, 298K) of **4b**.

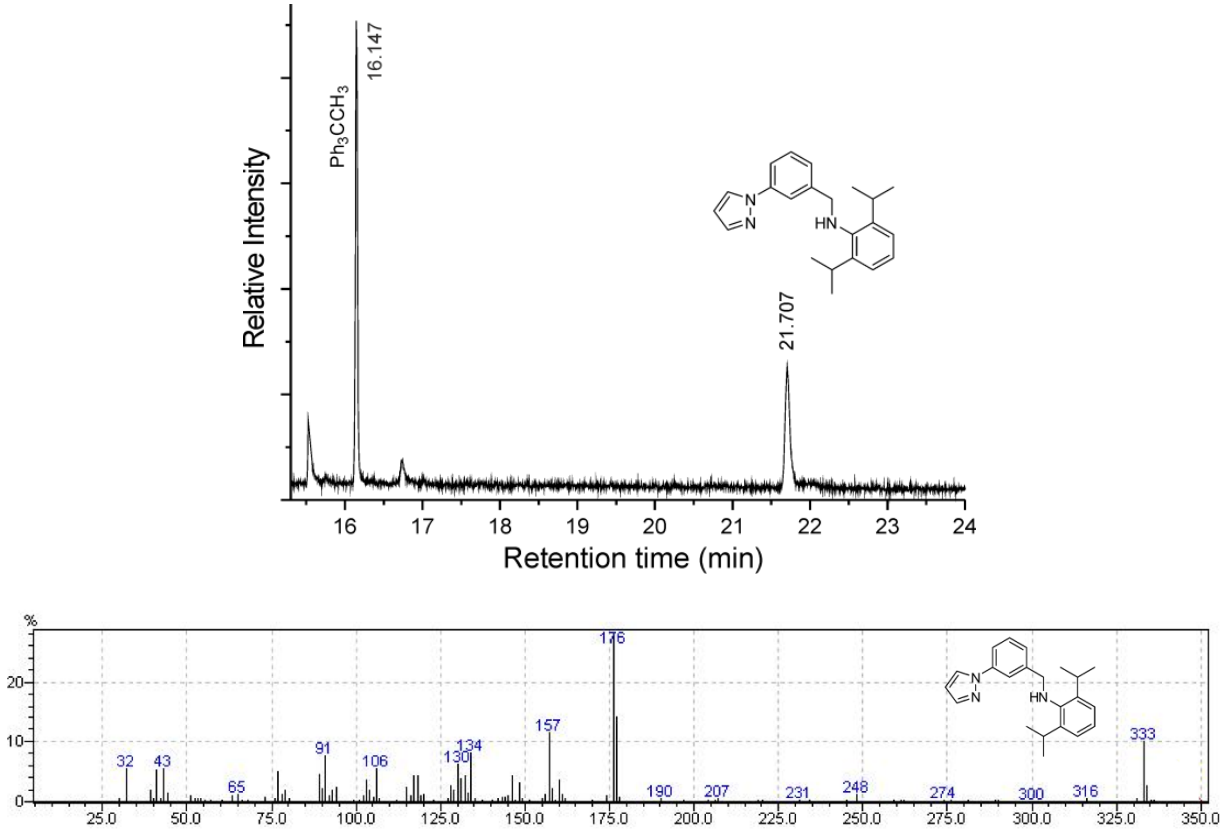
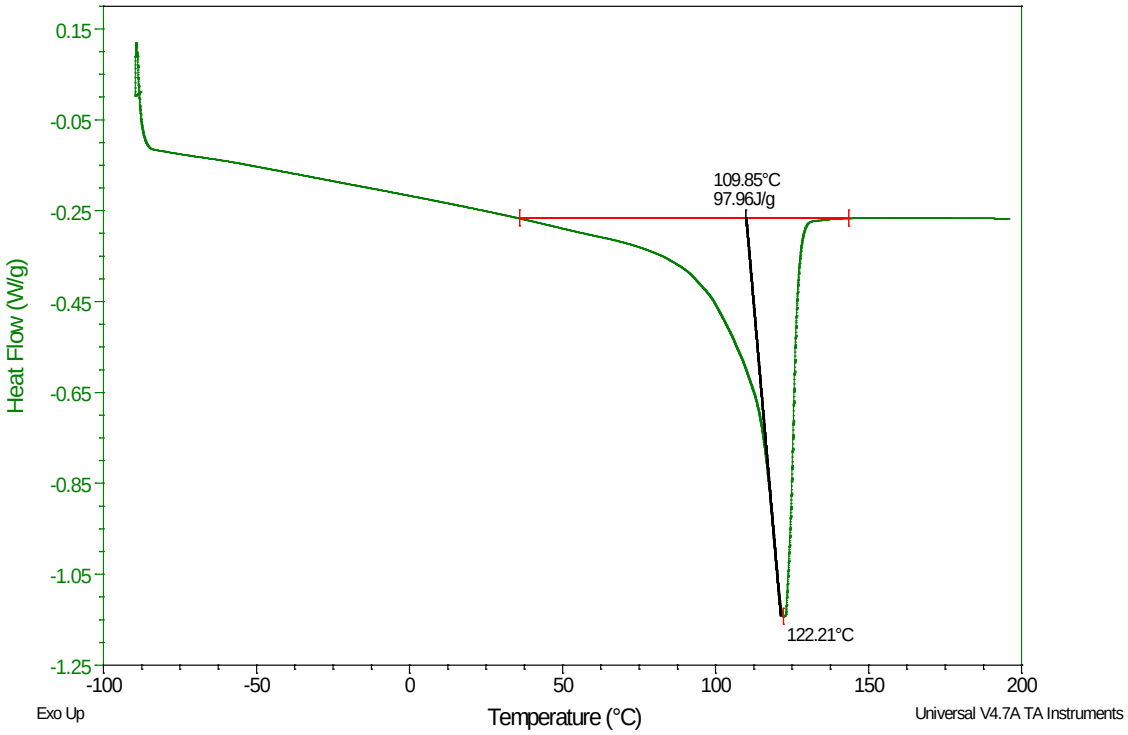


Fig. S16. GC trace of the reaction solution (catalyst **3a**:monomer 1:1) after quenching with MeOH (GC program: 40°C/1min, 15°C/min, 250°C/20min) and relative MS chromatogram at 21.7 min.



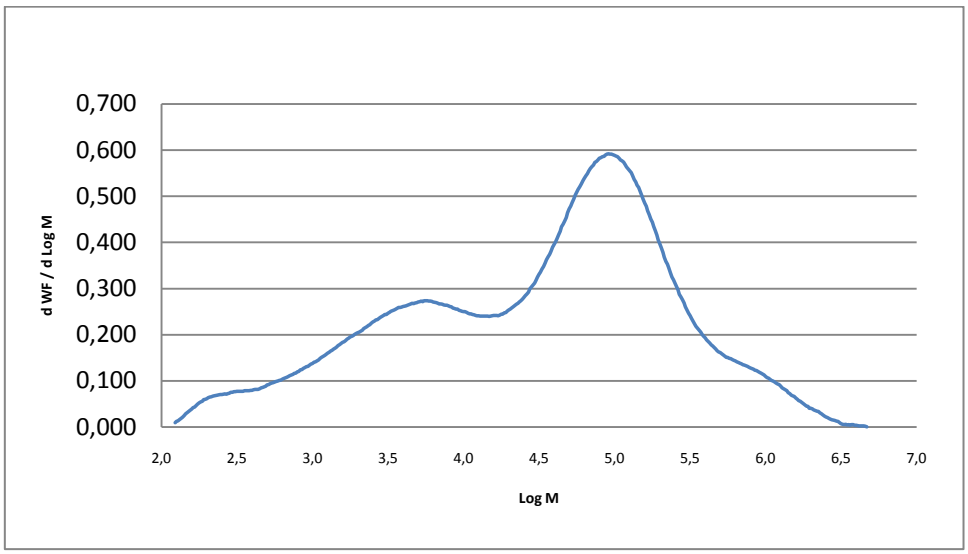
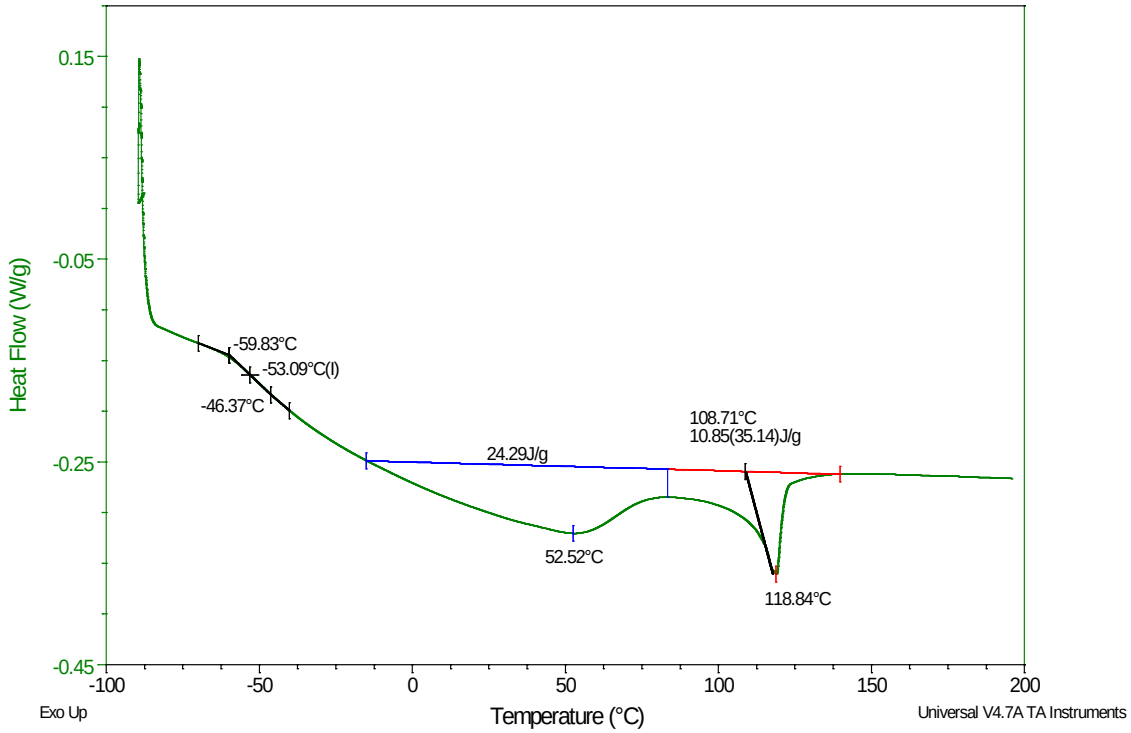


Fig. S17. DSC and GPC for ethylene/1-octene copolymer prepared by **3.**



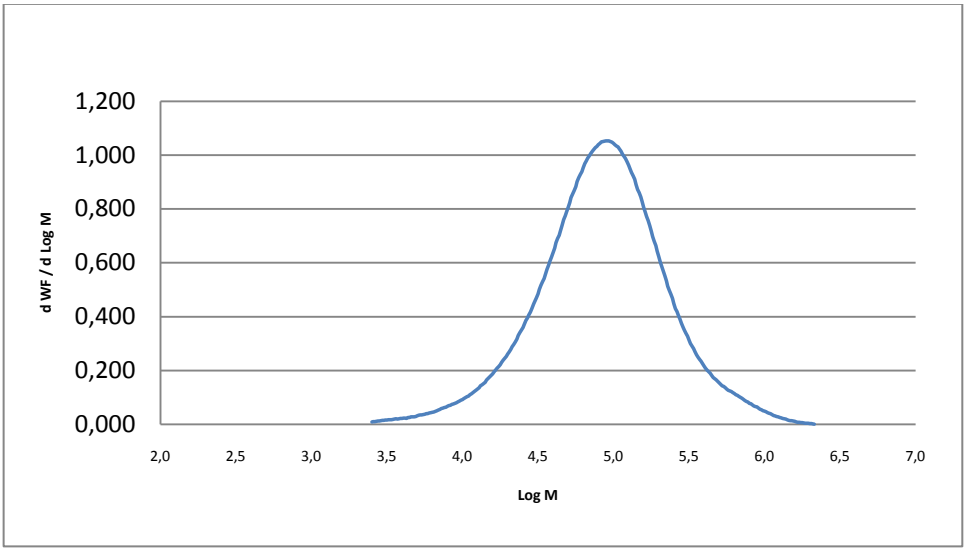


Fig. S18. DSC and GPC for ethylene/1-octene copolymer prepared by **4.**

Table S1. Crystal data and structure refinement for **4**.

Identification code	**4**	
Empirical formula	$C_{24}H_{31}HfN_3$	
Formula weight	540.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 10.5097(2) Å	α= 90°
	b = 12.3812(2) Å	β= 90°
	c = 33.8422(5) Å	γ = 90°
Volume	4403.64(13) $Å^3$	
Z	8	
Density (calculated)	1.629 Mg/m^3	
Absorption coefficient	4.751 mm^{-1}	
F(000)	2144	
Crystal size	0.220 x 0.220 x 0.040 mm^3	
Theta range for data collection	1.203 to 27.5°	
Index ranges	-12<=h<=13, -16<=k<=16, -43<=l<=43	
Reflections collected	51747	
Independent reflections	4968 [R(int) = 0.0278]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4968 / 0 / 259	
Goodness-of-fit on F^2	1.199	
Final R indices [I>2sigma(I)]	R1 = 0.0207, wR2 = 0.0375	
R indices (all data)	R1 = 0.0258, wR2 = 0.0387	
Largest diff. peak and hole	0.643 and -1.670 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Hf(1)	2075(1)	6673(1)	1595(1)	9(1)
N(1)	963(2)	5814(2)	1203(1)	10(1)
N(2)	1850(2)	6268(2)	2528(1)	12(1)
N(3)	2537(2)	6855(2)	2260(1)	12(1)
C(1)	970(2)	5502(2)	1955(1)	11(1)
C(2)	94(3)	4837(2)	1762(1)	12(1)
C(3)	-796(3)	4244(2)	1979(1)	15(1)
C(4)	-815(3)	4330(2)	2390(1)	16(1)
C(5)	50(3)	4985(2)	2591(1)	15(1)
C(6)	927(3)	5542(2)	2365(1)	12(1)
C(7)	175(3)	4875(2)	1316(1)	14(1)
C(8)	811(3)	6106(2)	794(1)	11(1)
C(9)	1721(3)	5790(2)	510(1)	12(1)
C(10)	1522(3)	6076(2)	115(1)	16(1)
C(11)	474(3)	6666(2)	-1(1)	18(1)
C(12)	-418(3)	6974(2)	278(1)	15(1)
C(13)	-277(3)	6702(2)	675(1)	13(1)
C(14)	2867(3)	5108(2)	614(1)	15(1)
C(15)	-1324(3)	7018(2)	963(1)	16(1)
C(16)	4101(3)	5566(3)	442(1)	25(1)
C(17)	2680(3)	3937(2)	476(1)	27(1)
C(18)	-1575(3)	8235(2)	967(1)	24(1)
C(19)	-2563(3)	6414(3)	867(1)	26(1)
C(20)	3366(3)	7425(2)	2472(1)	16(1)
C(21)	3221(3)	7211(2)	2875(1)	18(1)
C(22)	2251(3)	6468(2)	2898(1)	15(1)
C(23)	4147(3)	6580(2)	1437(1)	16(1)
C(24)	1430(3)	8385(2)	1556(1)	17(1)

Table S3. Bond lengths [Å] and angles [°] for **4**.

Hf(1)-N(1)	2.062(2)
Hf(1)-C(1)	2.223(3)
Hf(1)-C(24)	2.229(3)
Hf(1)-C(23)	2.245(3)
Hf(1)-N(3)	2.313(2)
N(1)-C(8)	1.440(3)
N(1)-C(7)	1.477(3)
N(2)-C(22)	1.345(3)
N(2)-N(3)	1.368(3)
N(2)-C(6)	1.431(3)
N(3)-C(20)	1.333(3)
C(1)-C(6)	1.387(3)
C(1)-C(2)	1.397(4)
C(2)-C(3)	1.397(4)
C(2)-C(7)	1.514(3)
C(3)-C(4)	1.396(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.395(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.384(4)
C(5)-H(5)	0.9500
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.411(4)
C(8)-C(13)	1.420(4)
C(9)-C(10)	1.399(4)
C(9)-C(14)	1.512(4)
C(10)-C(11)	1.378(4)
C(10)-H(10)	0.9500
C(11)-C(12)	1.385(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.392(3)
C(12)-H(12)	0.9500
C(13)-C(15)	1.521(4)
C(14)-C(16)	1.529(4)
C(14)-C(17)	1.536(4)

C(14)-H(14)	1.0000
C(15)-C(18)	1.530(4)
C(15)-C(19)	1.536(4)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(21)	1.396(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.376(4)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
N(1)-Hf(1)-C(1)	73.75(9)
N(1)-Hf(1)-C(24)	106.28(9)
C(1)-Hf(1)-C(24)	119.60(10)
N(1)-Hf(1)-C(23)	111.77(9)
C(1)-Hf(1)-C(23)	127.12(10)
C(24)-Hf(1)-C(23)	109.25(10)
N(1)-Hf(1)-N(3)	142.58(8)
C(1)-Hf(1)-N(3)	68.84(8)
C(24)-Hf(1)-N(3)	91.63(8)
C(23)-Hf(1)-N(3)	91.84(9)
C(8)-N(1)-C(7)	112.6(2)

C(8)-N(1)-Hf(1)	123.45(16)
C(7)-N(1)-Hf(1)	123.88(15)
C(22)-N(2)-N(3)	110.7(2)
C(22)-N(2)-C(6)	133.4(2)
N(3)-N(2)-C(6)	115.9(2)
C(20)-N(3)-N(2)	105.6(2)
C(20)-N(3)-Hf(1)	135.59(18)
N(2)-N(3)-Hf(1)	118.80(16)
C(6)-C(1)-C(2)	117.8(2)
C(6)-C(1)-Hf(1)	122.79(19)
C(2)-C(1)-Hf(1)	118.20(18)
C(3)-C(2)-C(1)	120.4(2)
C(3)-C(2)-C(7)	125.3(2)
C(1)-C(2)-C(7)	114.2(2)
C(4)-C(3)-C(2)	119.4(3)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(5)-C(4)-C(3)	121.5(2)
C(5)-C(4)-H(4)	119.3
C(3)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	117.0(2)
C(6)-C(5)-H(5)	121.5
C(4)-C(5)-H(5)	121.5
C(5)-C(6)-C(1)	123.9(2)
C(5)-C(6)-N(2)	123.4(2)
C(1)-C(6)-N(2)	112.7(2)
N(1)-C(7)-C(2)	108.3(2)
N(1)-C(7)-H(7A)	110.0
C(2)-C(7)-H(7A)	110.0
N(1)-C(7)-H(7B)	110.0
C(2)-C(7)-H(7B)	110.0
H(7A)-C(7)-H(7B)	108.4
C(9)-C(8)-C(13)	119.8(2)
C(9)-C(8)-N(1)	120.7(2)
C(13)-C(8)-N(1)	119.5(2)
C(10)-C(9)-C(8)	118.7(2)
C(10)-C(9)-C(14)	118.8(2)
C(8)-C(9)-C(14)	122.4(2)

C(11)-C(10)-C(9)	121.6(3)
C(11)-C(10)-H(10)	119.2
C(9)-C(10)-H(10)	119.2
C(10)-C(11)-C(12)	119.6(2)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(11)-C(12)-C(13)	121.3(3)
C(11)-C(12)-H(12)	119.3
C(13)-C(12)-H(12)	119.3
C(12)-C(13)-C(8)	119.0(2)
C(12)-C(13)-C(15)	118.6(2)
C(8)-C(13)-C(15)	122.4(2)
C(9)-C(14)-C(16)	112.4(2)
C(9)-C(14)-C(17)	110.8(2)
C(16)-C(14)-C(17)	110.1(2)
C(9)-C(14)-H(14)	107.8
C(16)-C(14)-H(14)	107.8
C(17)-C(14)-H(14)	107.8
C(13)-C(15)-C(18)	112.5(2)
C(13)-C(15)-C(19)	110.6(2)
C(18)-C(15)-C(19)	109.6(2)
C(13)-C(15)-H(15)	108.0
C(18)-C(15)-H(15)	108.0
C(19)-C(15)-H(15)	108.0
C(14)-C(16)-H(16A)	109.5
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(14)-C(17)-H(17A)	109.5
C(14)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(14)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5

H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(15)-C(19)-H(19A)	109.5
C(15)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(15)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(3)-C(20)-C(21)	110.8(3)
N(3)-C(20)-H(20)	124.6
C(21)-C(20)-H(20)	124.6
C(22)-C(21)-C(20)	105.2(2)
C(22)-C(21)-H(21)	127.4
C(20)-C(21)-H(21)	127.4
N(2)-C(22)-C(21)	107.7(2)
N(2)-C(22)-H(22)	126.1
C(21)-C(22)-H(22)	126.1
Hf(1)-C(23)-H(23A)	109.5
Hf(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Hf(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Hf(1)-C(24)-H(24A)	109.5
Hf(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Hf(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Hf(1)	10(1)	10(1)	8(1)	0(1)	1(1)	-1(1)
N(1)	11(1)	10(1)	9(1)	1(1)	1(1)	-1(1)
N(2)	14(1)	13(1)	9(1)	0(1)	1(1)	2(1)
N(3)	12(1)	12(1)	14(1)	0(1)	1(1)	0(1)
C(1)	8(1)	12(1)	12(1)	0(1)	2(1)	2(1)
C(2)	13(1)	10(1)	12(1)	1(1)	0(1)	2(1)
C(3)	14(1)	11(1)	18(1)	3(1)	0(1)	0(1)
C(4)	16(2)	14(1)	19(1)	6(1)	6(1)	0(1)
C(5)	21(2)	14(1)	11(1)	2(1)	4(1)	4(1)
C(6)	14(1)	10(1)	13(1)	1(1)	-1(1)	3(1)
C(7)	17(1)	12(1)	14(1)	1(1)	-1(1)	-3(1)
C(8)	13(1)	9(1)	11(1)	0(1)	-1(1)	-3(1)
C(9)	14(1)	11(1)	12(1)	-1(1)	-1(1)	-1(1)
C(10)	18(2)	20(1)	10(1)	-1(1)	2(1)	1(1)
C(11)	21(2)	24(1)	10(1)	5(1)	-2(1)	-1(1)
C(12)	13(1)	16(1)	16(1)	3(1)	-3(1)	1(1)
C(13)	13(1)	12(1)	13(1)	-1(1)	0(1)	-1(1)
C(14)	16(2)	17(1)	12(1)	-4(1)	0(1)	2(1)
C(15)	13(2)	21(1)	14(1)	1(1)	1(1)	4(1)
C(16)	17(2)	40(2)	18(1)	0(1)	1(1)	5(1)
C(17)	35(2)	19(2)	27(2)	-9(1)	-13(1)	12(1)
C(18)	28(2)	23(1)	21(1)	-2(1)	0(1)	12(1)
C(19)	15(2)	34(2)	27(2)	4(1)	2(1)	-1(1)
C(20)	13(1)	16(1)	20(1)	-3(1)	-2(1)	1(1)
C(21)	20(2)	17(1)	16(1)	-6(1)	-5(1)	6(1)
C(22)	21(2)	15(1)	9(1)	-2(1)	-2(1)	7(1)
C(23)	14(1)	20(1)	15(1)	-1(1)	3(1)	-3(1)
C(24)	24(2)	13(1)	13(1)	1(1)	0(1)	-1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **4**.

	x	y	z	U(eq)
H(3)	-1384	3785	1847	18
H(4)	-1429	3934	2536	19
H(5)	38	5045	2871	18
H(7A)	563	4202	1215	17
H(7B)	-687	4946	1201	17
H(10)	2125	5859	-79	19
H(11)	363	6859	-270	22
H(12)	-1140	7379	198	18
H(14)	2950	5102	908	18
H(15)	-1049	6799	1234	19
H(16A)	4081	5510	154	38
H(16B)	4826	5155	545	38
H(16C)	4187	6326	519	38
H(17A)	1921	3634	602	41
H(17B)	3427	3508	549	41
H(17C)	2572	3923	188	41
H(18A)	-782	8619	1025	36
H(18B)	-2208	8404	1171	36
H(18C)	-1896	8462	708	36
H(19A)	-2875	6644	607	39
H(19B)	-3204	6579	1068	39
H(19C)	-2400	5635	863	39
H(20)	3973	7912	2365	20
H(21)	3692	7513	3088	21
H(22)	1923	6153	3132	18
H(23A)	4424	5825	1441	24
H(23B)	4644	6995	1630	24
H(23C)	4278	6881	1173	24
H(24A)	1299	8580	1278	25
H(24B)	2079	8858	1671	25
H(24C)	629	8469	1701	25

Table S6. Torsion angles [°] for **4**.

C(22)-N(2)-N(3)-C(20)	-0.2(3)
C(6)-N(2)-N(3)-C(20)	-177.0(2)
C(22)-N(2)-N(3)-Hf(1)	179.59(16)
C(6)-N(2)-N(3)-Hf(1)	2.8(3)
C(6)-C(1)-C(2)-C(3)	0.5(4)
Hf(1)-C(1)-C(2)-C(3)	-167.35(19)
C(6)-C(1)-C(2)-C(7)	177.7(2)
Hf(1)-C(1)-C(2)-C(7)	9.9(3)
C(1)-C(2)-C(3)-C(4)	0.8(4)
C(7)-C(2)-C(3)-C(4)	-176.2(3)
C(2)-C(3)-C(4)-C(5)	-0.9(4)
C(3)-C(4)-C(5)-C(6)	-0.1(4)
C(4)-C(5)-C(6)-C(1)	1.5(4)
C(4)-C(5)-C(6)-N(2)	178.2(2)
C(2)-C(1)-C(6)-C(5)	-1.6(4)
Hf(1)-C(1)-C(6)-C(5)	165.6(2)
C(2)-C(1)-C(6)-N(2)	-178.7(2)
Hf(1)-C(1)-C(6)-N(2)	-11.5(3)
C(22)-N(2)-C(6)-C(5)	12.1(4)
N(3)-N(2)-C(6)-C(5)	-172.0(2)
C(22)-N(2)-C(6)-C(1)	-170.9(3)
N(3)-N(2)-C(6)-C(1)	5.0(3)
C(8)-N(1)-C(7)-C(2)	-163.5(2)
Hf(1)-N(1)-C(7)-C(2)	12.9(3)
C(3)-C(2)-C(7)-N(1)	163.5(2)
C(1)-C(2)-C(7)-N(1)	-13.6(3)
C(7)-N(1)-C(8)-C(9)	-100.3(3)
Hf(1)-N(1)-C(8)-C(9)	83.2(3)
C(7)-N(1)-C(8)-C(13)	78.6(3)
Hf(1)-N(1)-C(8)-C(13)	-97.8(3)
C(13)-C(8)-C(9)-C(10)	0.0(4)
N(1)-C(8)-C(9)-C(10)	178.9(2)
C(13)-C(8)-C(9)-C(14)	-177.0(2)
N(1)-C(8)-C(9)-C(14)	2.0(4)
C(8)-C(9)-C(10)-C(11)	0.7(4)
C(14)-C(9)-C(10)-C(11)	177.8(3)

C(9)-C(10)-C(11)-C(12)	-0.8(4)
C(10)-C(11)-C(12)-C(13)	0.1(4)
C(11)-C(12)-C(13)-C(8)	0.6(4)
C(11)-C(12)-C(13)-C(15)	-177.0(3)
C(9)-C(8)-C(13)-C(12)	-0.6(4)
N(1)-C(8)-C(13)-C(12)	-179.6(2)
C(9)-C(8)-C(13)-C(15)	176.8(2)
N(1)-C(8)-C(13)-C(15)	-2.1(4)
C(10)-C(9)-C(14)-C(16)	50.7(3)
C(8)-C(9)-C(14)-C(16)	-132.3(3)
C(10)-C(9)-C(14)-C(17)	-72.9(3)
C(8)-C(9)-C(14)-C(17)	104.1(3)
C(12)-C(13)-C(15)-C(18)	-57.9(3)
C(8)-C(13)-C(15)-C(18)	124.6(3)
C(12)-C(13)-C(15)-C(19)	65.1(3)
C(8)-C(13)-C(15)-C(19)	-112.4(3)
N(2)-N(3)-C(20)-C(21)	0.0(3)
Hf(1)-N(3)-C(20)-C(21)	-179.75(19)
N(3)-C(20)-C(21)-C(22)	0.2(3)
N(3)-N(2)-C(22)-C(21)	0.3(3)
C(6)-N(2)-C(22)-C(21)	176.4(3)
C(20)-C(21)-C(22)-N(2)	-0.3(3)

Symmetry transformations used to generate equivalent atoms: